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THE DEPENDENCE OF THE SPEED OF HYDROGEN EXCHANGE ON THE CHARACTER OF THE BOND

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/This article reports on a series of investigations the results of which can be used in the enrichment of heavy hydrogen isotopes./

In a previous paper by the author (Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk, No 1, 1949) the assumption was made that the strongly retarded exchange of hydrogen isotopes at the C - H bonds is not due to the special strength of these bonds, but to the fact that in compounds in which all four electron pairs around the carbon atom are occupied, the breaking of one of the C - H bonds is required, for which a large amount of activation energy is needed. On the contrary, in the presence of a free pair of electrons, the adding of an atom of D and the removal of an atom of H take place simultaneously.

For the experimental confirmation of this assumption, the author cited the results of the studies of exchange at N - H, P - H, and Si - H bonds in such compounds where the central atom, as well as the carbon atom, are fully surrounded by blocked electron pairs. In accordance with this assumption, the exchange at the bonds in question is slowed down or does not take place at all, showing the same peculiarities as the exchange at C - H bonds of organic compounds.

In ammonium salts the exchange of hydrogen isotopes with concentrated solutions of heavy water does not take place instantaneously, as was held earlier, but with a measurable speed that is greatly reduced in the presence of free acids, which suppress hydrolysis.

In the experiments of the author and his co-workers, a very slow exchange of hydrogen for deuterium was discovered in salts of hypophosphoric acid (the data of Erlenmeyer and Gaertner on the complete absence of exchange in

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potassium and barium salts turned out to be erroneous) and quick exchange of all three hydrogen atoms in free hypophosphoric acid is easily explained by the existence of two tautomeric forms of acid which are in equilibrium: $HO(H_2P:O) \rightleftharpoons (HO)_2PH$ and by the reversible hydrolysis of its salts. Of these forms, the latter has a free electron pair and therefore easily exchanges hydrogen atoms.

The absence of exchange of hydrogen with deuterium in triethyl silane and triphenyl silane, as established by the author and his co-workers, is explained by the absence of free pairs of electrons in organic silicon compounds. This also explains the complete absence of exchange, or slow exchange of HDO and molecular hydrogen with ammonium complexes of cobalt, well known in literature, and also the absence of exchange between $B_2H_6 \cdot 2NH_3$ and ND_3. On the other hand, all compounds having free electrons at the atom bound to hydrogen easily exchange the latter for deuterium.

From all these facts it is obvious that the character of hydrogen exchange at H - X bonds is determined not only by the nature of the X atom, as generally believed, but by the combination of all its bonds in the given molecule.

The study of hydrogen exchange in the methyl group of salts of acetic acid with heavy water showed a strong dependence of the speed of the exchange on the nature of the cations. The speed of the exchange increases parallel to the degree of the covalence of the O - X bond (where X is the cation replacing the hydrogen in the carboxyl radical). The exchange in salts can be ascribed neither to free acetic acid, produced as a result of hydrolysis, nor to the acetate anion. Apparently, it originates, basically, in the nondissociated molecules of the salt or in the anions of the acid, which are polarized by the adjacent cations.

According to these considerations, lead acetate, containing a covalent O - Pb bond, can be considered an analogue of an ester of acetic acid, and therefore should exhibit addition reactions characteristic of acetic and alkyl esters, i.e. proceeding with the breaking of the CH_3CO - OPb bond, as in esters.

These assumptions were confirmed by condensation reactions of lead salts with anilide, benzaldehyde, and m-nitrobenzaldehyde and the absence of these reactions in acetic acid and its alkali metal salts which have no clearly expressed convalent bonds.

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